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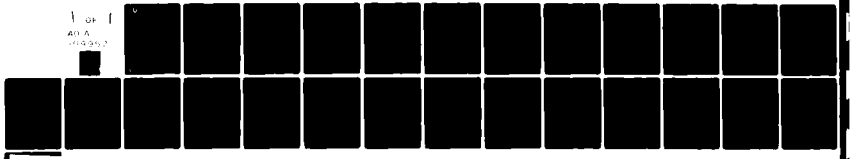

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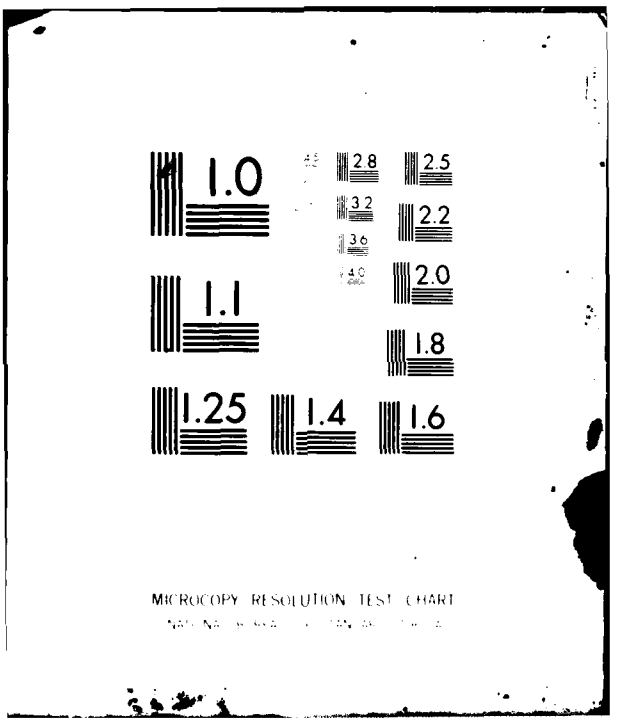
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RESEARCH AND DEVELOPMENT TECHNICAL REPORT

DELET-TR-81-18

MAGNETOCRYSTALLINE ANISOTROPY IN THE SYSTEMS SAMARIUM-COBALT-IRON AND SAMARIUM-MANGANESE-COBALT-IRON.

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SEPTEMBER 1981

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18. SUPPLEMENTARY NOTES

*This work is part of an ongoing effort in our laboratory to develop high-energy-product permanent magnet materials for use in advanced millimeter-wave/microwave systems.

19. KEY WORDS *(Continue on reverse side if necessary and identify by block number)*

Anisotropy, Coercivity, Crystalline Fields, Energy Product, Saturation Magnetization

20. ABSTRACT *(Continue on reverse side if necessary and identify by block number)*

The anisotropy fields (H_A) and saturation magnetizations ($4\pi M_s$) of the systems $Sm_2(Co_{1-x}Fe_x)_{17}$ and $Sm_2Mn(Co_{1-x}Fe_x)_{16}$ were measured at 4.2 K and 300 K in applied fields up to 100 kOe. The presence of the Mn in the latter system raised the anisotropy fields by as much as 55% over those measured for the corresponding compounds in the ternary system. The augmentation of anisotropy was accompanied by a slight decline in $4\pi M_s$ of approximately 5% for the materials of highest H_A. The values of $4\pi M_s$ for the quaternary compounds showed much less temperature dependence, increasing by

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about 5% in going from 300 K to 4.2 K as compared to 15% for the ternary system. A comparison of the present H_A results with previous anisotropy measurements of Perkins and Strässler, obtained by extrapolation from applied fields up to 20 kOe, showed the latter to be too low by as much as 50%. The effect of the higher H_A values on the anisotropy constant K_1 and the crystal field parameter $\langle r \rangle A_2^0$ will be presented and the consequences discussed.

CONTENTS

INTRODUCTION

In a recent paper by Perkins and Strässler[1] (P-S), anisotropy measurements on the pseudobinary $Sm_2(Co,M)_{17}$ compounds, where M = Fe, Mn or Cr, were presented. These data were analyzed by the application of crystal field theory to obtain a quantitative measure of how the dominant samarium contribution to the anisotropy is affected by M-atom substitutions for the cobalt. The quantitative result was given in terms of the crystal field parameter $\langle r^2 \rangle A_2^0 \simeq -\Delta K_1(0)$, where the stabilization energy $\Delta K_1(0)$ is the difference between the anisotropy constant $K_1(0)$ at absolute zero for a given samarium compound, $Sm_2(Co_{1-x}M_x)_{17}$, and that for the corresponding yttrium compound, $Y_2(Co_{1-x}M_x)_{17}$. It was assumed that the transition-metal sublattice is essentially the same in $Sm_2(Co,M)_{17}$ and $Y_2(Co,M)_{17}$. Therefore, its contribution to the overall anisotropy will be the same in both compounds. By subtraction, the crystal field contribution of the Sm^{3+} ion in the Sm compounds may be deduced, since it is further assumed that the nonmagnetic yttrium ion makes no contribution.

P-S anisotropy data were taken in magnetic fields up to 20 kOe. Recently, we measured some of the same alloys in fields up to 100 kOe and found higher values for the anisotropy fields H_A from which the anisotropy constants K_1 are derived, since $K_1 = H_A M_s/2$. We wish to emphasize the difficulties inherent in long extrapolations such as P-S used. We show how these can lead to large underestimations for the anisotropy constants and the crystal field parameters by comparing our results with those of P-S for the $Sm_2(Co_{1-x}Fe_x)_{17}$ system. We also report some new results for the quaternary system $Sm_2Mn(Co_{1-x}Fe_x)_{16}$ which imply that these materials are promising for permanent magnet applications.

There are many desired permanent magnet applications for millimeter wave and microwave devices which are presently not viable because of stringent performance requirements coupled with severe restrictions on weight and bulk.[2,3] Many of these conditions could be satisfied by the commercial availability of permanent magnet materials with energy products in excess of 30 MGOe. At present, the $Sm_2(Co,M)_{17}$ compounds with their high molecular moments seem to show the greatest promise. Ray and Strnat[4-6] have pointed to the $Sm_2(Co_{1-x}Fe_x)_{17}$ system as being potentially suitable for high energy product, high coercive force, permanent magnet applications

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2. F. Rothwarf, H. A. Leupold, J. L. Jasper, Jr., Proc. of the Third International Workshop on Rare Earth-Cobalt Magnets and Their Applications, Univ. of California, San Diego, June 27-30, 1978; printed by the Univ. of Dayton School of Engineering, K. J. Strnat, ed., p. 255.

3. H. A. Leupold and F. Rothwarf, "Design of Biasing Magnets for E-F and I-J Band Cross-Field Amplifier Tubes," ERADCOM Tech Report, DELET-TR-78-12, June 1978.

4. A. E. Ray and K. J. Strnat, Tech. Report AFML-TR-72-99 (Wright-Patterson Air Force Base, Ohio, April 1972), p.29.

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6. A. E. Ray and K. J. Strnat, "Metallurgical and Magnetic Properties of the Intermetallic Phases $R_2(Co,Fe)_{17}$," 7th Conference on Rare-Earth Metals, Alloys & Compounds, Paper 15, Moscow, September 1972.

in that its alloys have high saturation magnetizations and Curie temperatures as well as large uniaxial magnetocrystalline anisotropies. The addition of iron to Sm_2Co_{17} increases $4\pi M_s$ to over 16 kG and offers the potential for an energy product $(BH)_{max}$ of over 40 MGOe.

Sm_2Co_{17} has a higher room temperature saturation magnetization $4\pi M_s$ ($\sim$ 13 kG)[5,7] than does $SmCo_5$ ($\sim$ 11 kG). However, its low anisotropy field, H_A (70-110 kOe),[5,7,8] as compared to $SmCo_5$ (with quotes as high as 350 kOe),[7] has discouraged its intensive development as a permanent magnet material, since a high H_A is a necessary (but not always sufficient) condition for attaining a high coercivity. For the three studies[7-9] that have already been made on the $Sm_2(Co_{1-x}Fe_x)_{17}$ system, it should be noted that the anisotropy fields do not agree in their absolute values[7,8] or in their composition dependence.[7-9] Some of the previous H_A data for the system are presented in Fig. 1. To resolve these discrepancies, it was decided to remeasure H_A for $Sm_2(Co_{1-x}Fe_x)_{17}$ in fields up to 100 kOe, thus eliminating reliance on the excessively long extrapolations heretofore used to obtain H_A.

During the course of a previous study of the magnetic anisotropy in the $Th(Co_{1-x}Fe_x)_5$ and $Y(Co_{1-x}Fe_x)_5$ systems,[10] F. Rothwarf et al had occasion to measure H_A for the compound $Sm_2Co_{16}Mn$, which had previously been studied by Schaller, Craig and Wallace (SCW).[11] H_A was found to be 150 kOe at room temperature. Since this was significantly higher than the values generally quoted for Sm_2Co_{17}, it was decided to initiate a magnetic anisotropy study of the quaternary system $Sm_2(Co_{1-x-y}Mn_yFe_x)_{17}$ where $(x + y) \leq 1$. The previous work of SCW[11] on $Sm_2Co_{17-x}Mn_x$ ($1 \leq x \leq 3$) indicated that the best technical results were achieved with $Sm_2Co_{16}Mn$. Thus, the initial quaternary system chosen for consideration was the one with $y = 0.0.588$, corresponding to the system $Sm_2Mn(Co_{1-x}Fe_x)_{16}$. In this paper we also present our encouraging results on this system.

EXPERIMENTAL

The various quaternary alloys were prepared by arc melting and rapid quenching in a copper hearth under argon or by induction melting in a boron nitride crucible with rapid quenching under argon. All starting metals were at least 99.9% pure. An attempt was made to homogenize each compound by annealing it in a tantalum container sealed into an evacuated quartz tube. The annealing temperatures ranged from 950-1000 C and were maintained from two to four weeks. All samples were checked by x-ray diffractometry to determine if they were single phase. Only results for the single phase materials are reported here.

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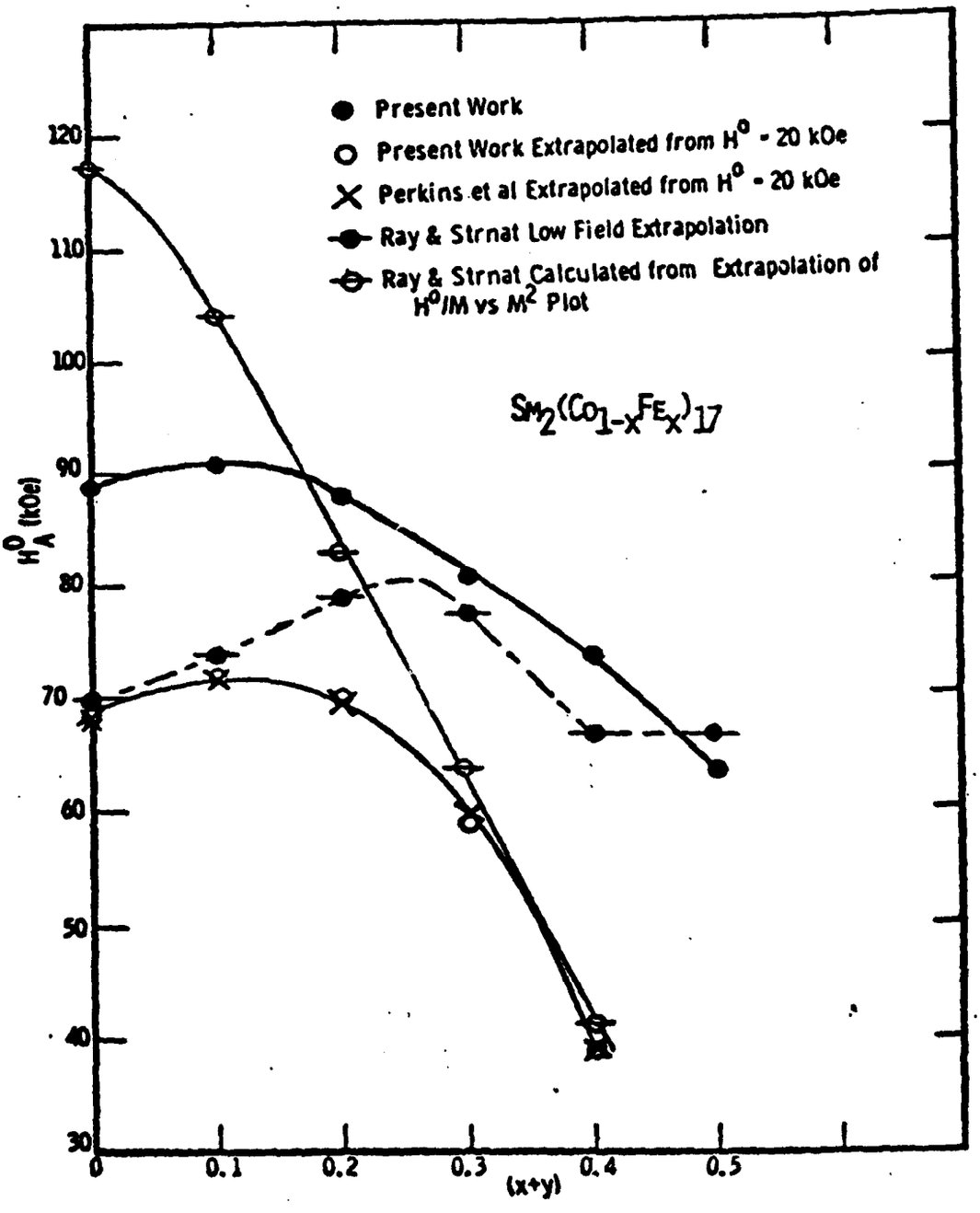

Figure 1. Uncorrected room temperature anisotropy fields (H_A^o) as a function from concentration in the system $Sm_2(Co_{1-x}Fe_x)_{17}$.

For the annealing procedure used, the single phase materials were those with the lower Fe concentrations up to $Sm_2MnCo_{10}Fe_6$. Reference to the phase diagrams for the Sm-Co[12] and Sm-Fe[13] systems makes it clear that a much higher annealing temperature, above 1200 C, followed by a rapid quench, would be necessary to obtain single phase samples of the iron-rich compounds. Cylindrical quaternary specimens were produced by suspending powders of the various compositions in an epoxy matrix and aligning them in a magnetic field while the epoxy hardened. Powder with grain sizes $\leq$ 37 μm was prepared by sifting material ground with a boron carbide mortar and pestle under argon in a glove box. The powder was thoroughly mixed with Shell B28 epoxy and Shell B40 hardener in a one-to-one ratio and poured into two identical cylinders. While the resin hardened in about one hour at a temperature of $\sim$ 100 C produced by heat gun, a field of 28 kOe was applied to orient the particles in one cylinder parallel to and in the other perpendicular to the cylinder axis. The anisotropy fields were determined from magnetization curves of the magnetically aligned cylinders.[14] The specimens of the ternary alloys were also in the form of powders suspended in epoxy cylinders and were obtained through the kindness of K. Strnat in whose laboratory they were prepared.

Magnetization curves (0-15 kOe) were obtained in the alignment direction and normal to it by means of a PAR vibrating sample magnetometer in the temperature interval from 4.2 to 300 K. The saturation magnetizations ($4\pi M_s$) were obtained from these data. The magnetization curves for the hard direction (0-100 kOe) were measured by means of a magnetometer employing an O.S. Walker Co. integrating fluxmeter and American Magnetics superconducting magnet.[15] The magnetization curves for the easy axis show saturation effects at low fields, whereas those for the hard axis are quite linear above 60 kOe. Extrapolation of the easy and hard axis curves to the point of their intersection gives an estimate of the anistropy field H_A. It should be noted that among the ternary compounds only Sm_2Co_{17} requires an extrapolation over an interval of more than 10% of the H_A value, and all compounds with $x > 0.1$ saturate at less than 100 kG and require no extrapolation. For the quaternaries, more extrapolations are required, but only for Sm_2MnCo_{16} does the extrapolation interval exceed 0.25 H_A. Because of imperfect alignment of the suspended particles in the epoxy based samples, the linear approach to saturation of the magnetization curve is relatively shallow for some samples, and thus contributes to extrapolation uncertainties as high as $\pm$ 10%. For this reason, as many as 20 determinations of H_A were made for samples in which long extrapolations were necessary, and an arithmetic mean of the results was taken to be the anisotropy field. For samples in which saturation was possible, measured values of H_A were generally reproducible to within one or two kG. Figure 2 illustrates both a saturated (A) and an extrapolated (B) curve.

Because of the large uncertainties encountered by previous investigators who relied on very long extrapolations ($\sim$ 0.8 H_A) to estimate H_A, demagnetization corrections were generally not attempted for specimens of cylindrical form. In the case of the present work, however, demagnetization corrections are in some instances larger than the experimental uncertainties. These corrections are very easily made when H_A is determined from cylindrical samples with their easy axes aligned along a diameter.[15] The external field H_A^0 is then applied along the cylinder axis to magnetize the sample in a hard direction. The applied field at which saturation

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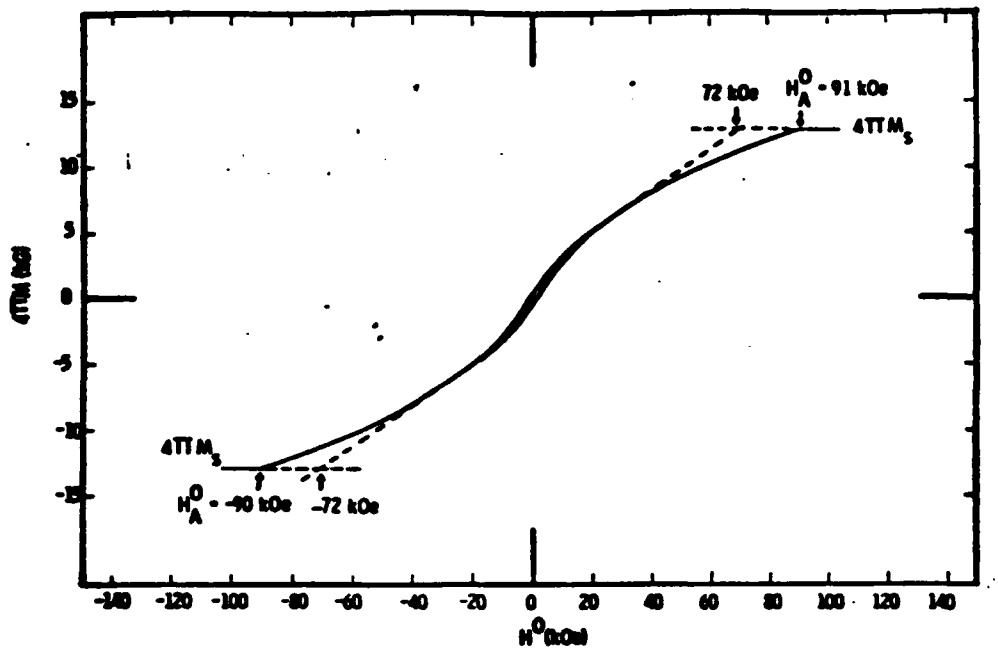
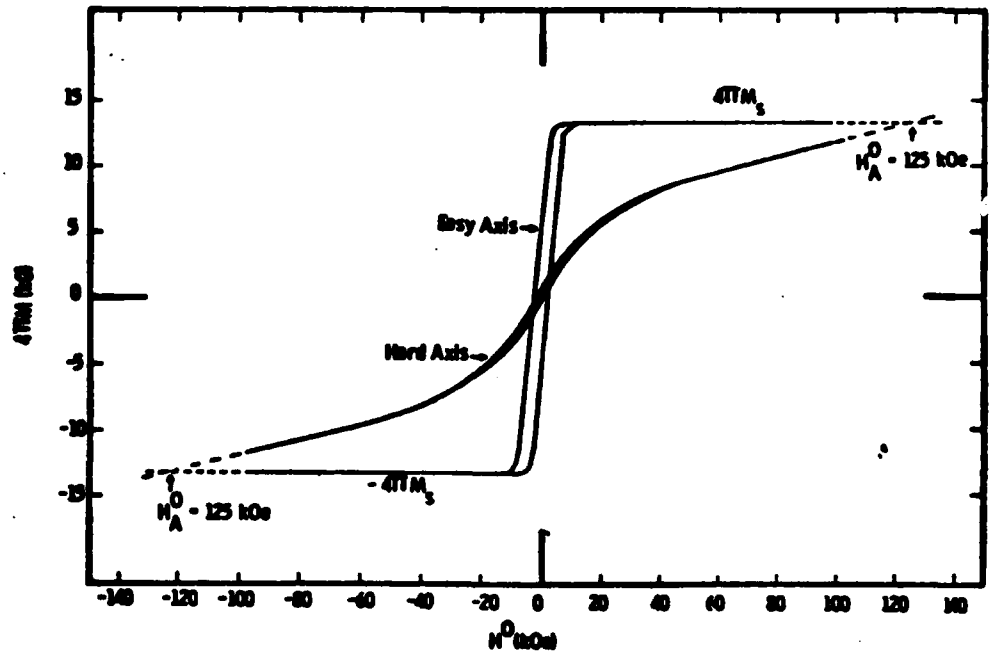
13. K. H. J. Buschow, J. Less-Common Metals 25, 131, (1971).
14. K. Strnat, G. Hoffer, J. C. Olson, W. Ostertag, and J. J. Becker, J. Appl. Phys. 38, 1001 (1967).
15. J.J. Winter, F. Rothwarf, H.A. Leupold, J.T. Breslin, Rev. Sci. Instrum. 49 845 (1978).



A shows the room temperature results for $Sm_2(Co_{0.9}Fe_{0.1})_{17}$ which was saturated. The dotted line indicates an extrapolation to $4\pi M_s$ from the neighborhood of H^O = 20 kOe with the resulting underestimate of H_A^O.



B illustrates an extrapolation of the He temperature magnetization curve of $Sm_2MnCo_{12}Fe_4$ to $4\pi M_s$ from the neighborhood of H^O = 100 kOe, the highest field obtainable in the present experiment.

Figure 2. Typical hard direction magnetization curves used to obtain H_A^O.

occurs is then taken to be the sum of the anisotropy field and the demagnetization field at the center of the cylinder because the center is where the total field is approximately the average field in the sample. Thus, to determine H_A, one need only find the field in a particle at the center of an axially saturated cylinder in an applied field H_A^o. H_A is then given by [15,16]

$$H_A = H_A^o - 4\pi S M_s \, 2/3 + 1/3S - (1+r^2)^{-1/2} \qquad (1)$$

where S is the ratio of powder to sample volume, r is the sample diameter to length ratio, and M_s is the saturation magnetization. An average spherical shape for the powder particles has been assumed. The rationale for this assumption has been given elsewhere.[16] The demagnetization corrections require that the raw anisotropy fields H_A^o be reduced by an average of about 5%

RESULTS

Figure 1 compares the room temperature anisotropy fields, H_A^o, measured in our experiments with the extrapolated values previously obtained by Perkins et al. on single crystal spheres and with those of Strnat et al. on epoxy-powder cylinders similar to those used in the present work. Since the latter results were uncorrected for demagnetization fields, H_A^o is plotted rather than H_A to provide a closer correspondence between the compared fields. It is clear that the values of H_A^o obtained by extensive direct extrapolation are much too low, although our overall curve shape is very similar to that obtained by Perkins et al.[7] The values deduced by Strnat from the anisotropy constants obtained from H/M vs M^2 plots are higher than those of the present work for $(x+y) < 0.2$ and lower for $(x+y) > 0.2$.

Figure 1 shows the values of H_A^o which would have been obtained, H_A^{*o}, had our room temperature magnetization curves been extrapolated from H = 20 kOe. (See Figure 2A for an example.) These are compared with the values of other investigators who used such an extrapolation. The results are in excellent accord with the work of Perkins et al.[7] Our results for the $Sm_2(Co_{1-x}Fe_x)_{17}$ system are summarized in Table I for 4.2 K and 300 K. Also presented are the H_A^{*o} values obtained on extrapolation from H = 20 kOe, as well as the ratios of H_A^{*o}/H_A^o. For the most part the H_A^o values shown were obtained with little or no extrapolation. It is apparent that the extrapolation from 20 kOe incurs considerable error, with the 4.2 K H_A^{*o} values displaying greater errors since a longer extrapolation was required. Clearly, these results illustrate the necessity of using applied fields as near to saturation as possible to avoid the substantial underestimations incurred by long extrapolations.

In Figure 3 the corrected H_A curves for the two systems are shown. The salient feature of Figure 3 is the dramatic increase of anisotropy field for $(x+y) \lesssim 0.4$, resulting from the presence of a single atom of manganese per formula unit.

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15. J. Winter, F. Rothwarf, H. A. Leupold, J. T. Breslin, Rev. Sci, Instrum. 49, 845 (1978).

16. H. A. Leupold, F. Rothwarf, J. J. Winter, A. Tauber, J. T. Breslin, and A. Schwartz, Proc. of the Second International Symposium on Magnetic Coercivity and Anisotropy of Rare Earth-Transition Metal Alloys, Univ. of California, San Diego, July 1, 1978; printed by Univ. of Dayton School of Engineering, K. J. Strnat, Ed., p 87.

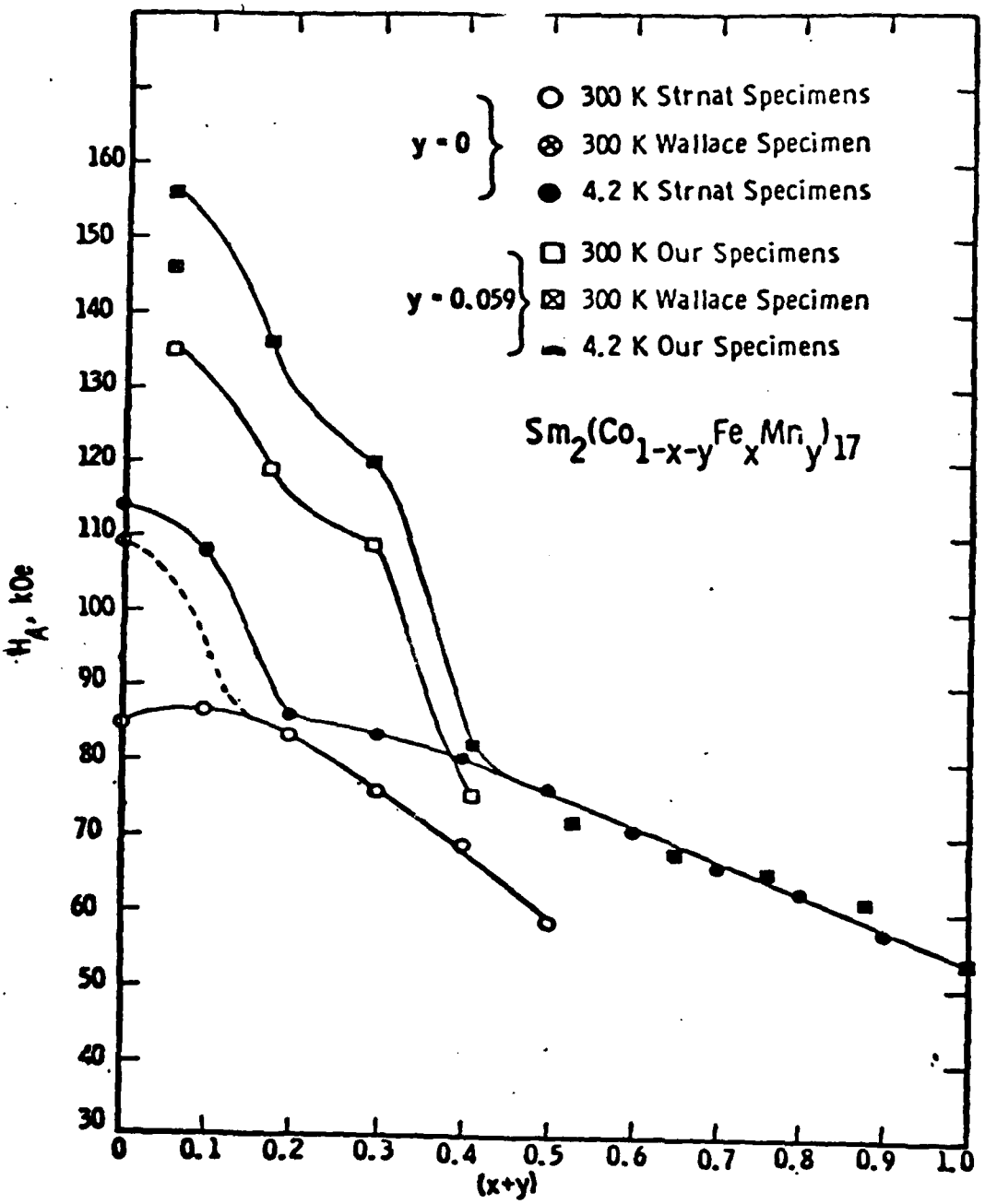

Figure 3. The anisotropy fields (H_A) of the system $Sm_2(Co_{1-x-y}Fe_xMn_y)_{17}$ for y=0 and y=0.059 at room and liquid helium temperatures as a function of the fraction of Co atoms replaced (x+y).

TABLE. ANISOTROPY FIELDS

COMPOUND	$T_r = 4.2$ K H_A^{o*}	H_A^o	H_A^{o*}/H_A^o	H_A^{o*}	H_A^o	H_A^{o*}/H_A^o
Sm_2Co_{17}	84	114	0.74	64	85	0.75
$Sm_2(Co_{0.9}Fe_{0.1})_{17}$	63	108	0.58	68	87	0.78
$Sm_2(Co_{0.8}Fe_{0.2})_{17}$	51	86	0.59	66	84	0.79
$Sm_2(Co_{0.7}Fe_{0.3})_{17}$	48	84	0.57	55	76	0.72
$Sm_2(Co_{0.6}Fe_{0.4})_{17}$	43	81	0.53	33	69	0.48

The increases were 35-40% at 4.2 K and 45-55% at room temperature. The experimental curves for the anisotropy fields of the ternary and quaternary compounds at 4.2 K are qualitatively similar to each other as well as to the room temperature quaternary curve. All three curves show the same initial steep decline in H_A with increasing replacement of cobalt with iron. The quaternary samples with $(x+y) \geq 0.5$ were not obtainable as single phase materials, and the results in these regions should not be taken too seriously. It is, however, interesting to note that H_A's measured for these materials tend to fall about the same straight line obtained from the measurements on the ternary compounds. This region of linear decline in H_A may be the result of a change from an easy axis to an easy plane regime at $(x+y) = 0.5$. Such a transformation is known to occur for the ternary system at room temperature,[4] but it is not certain whether such a change occurs at 4.2K.[17] It is curious that the room temperature curve for the ternary compounds differs qualitatively from that taken at 4.2 K, although no such difference is manifested by the quaternaries. Another Sm_2Co_{17} sample furnished by W. E. Wallace, previously measured at room temperature by Rothwarf, showed an H_A of 114 kOe as compared to the 88 kOe measured on the Strnat sample. If, however, one uses the measurement of Rothwarf on the Wallace sample of Sm_2Co_{17} as the true value of H_A, this anomalous aspect of the ternary curve disappears and the room temperature curve becomes more like that at 4.2 K (see the dashed line in Figure 3). Apparently, the behavior of H_A for this compound is very dependent on specimen preparation and/or stoichiometry.

The saturation magnetization ($4\pi M_s$) as a function of composition for room and liquid helium temperatures is shown in Figure 4. The curves for the ternary compounds show the same general shape commonly obtained for 2-17 compounds, except that the initial rise in magnetization with increasing iron content becomes much more abrupt in the vicinity of the easy-axis, easy-plane transformation at x=0.5. This abruptness occurs at both room temperature and at 4.2 K, even though the easy plane phase may not exist at liquid helium temperature. The saturation magnetizations of the quaternary compounds are, generally, somewhat smaller than those of their ternary counterparts, but Figure 4 shows there is little difference in the neighborhood of y=0.059, the region of highest anisotropy and, therefore, of greatest potential for permanent magnet application. The quaternary materials have the additional advantage of showing much less temperature variation of saturation magnetization $4\pi M_s$. For example, for $x+y < 0.5$, the spread between the ternary curves for

4. A. E. Ray and K. J. Strnat, Tech. Report AFML-TR-72-99 (Wright-Patterson Air Force Base, Ohio, April 1972), p. 29.

17. K. S. V. L. Narasimhan, private communication.

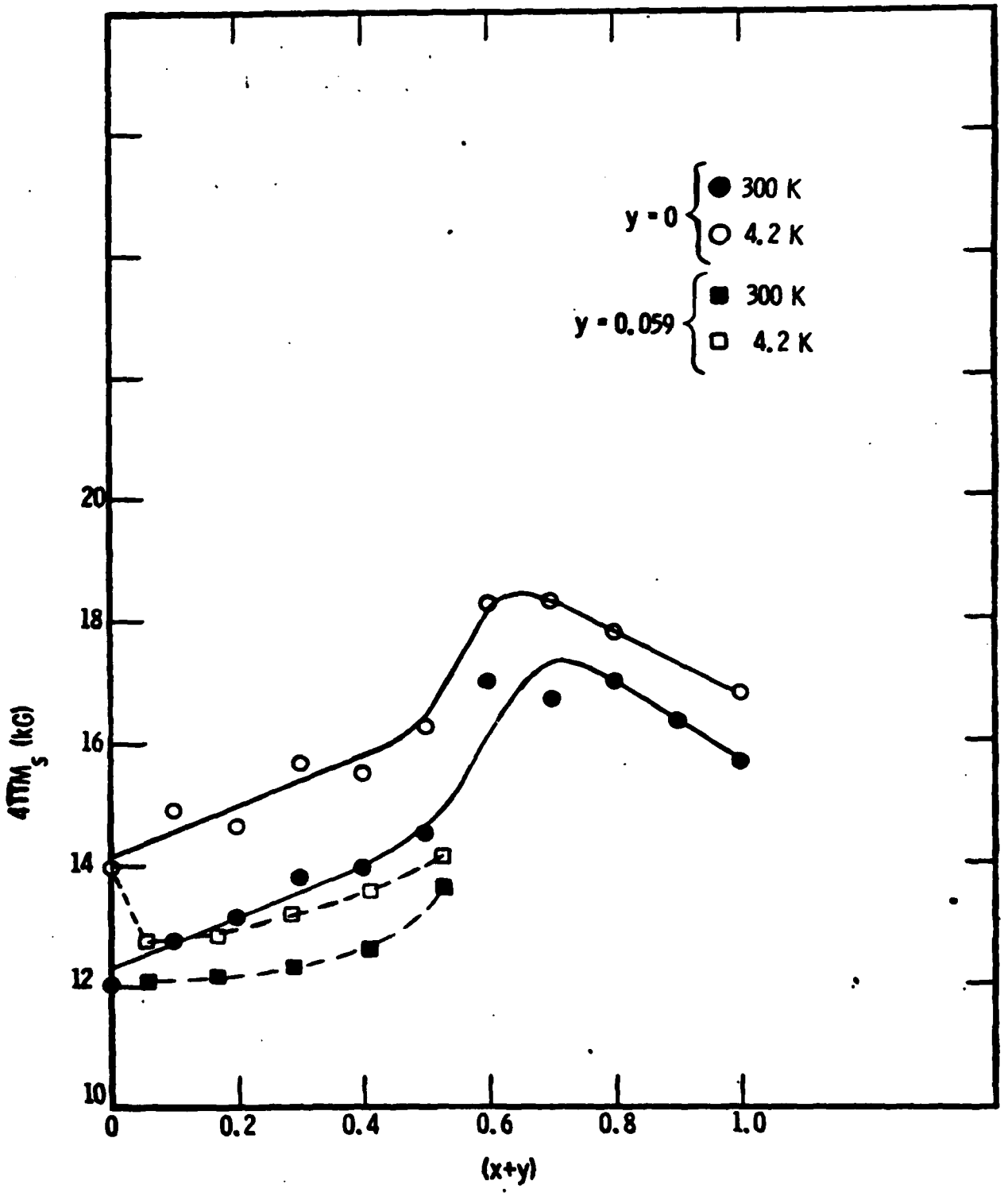

Figure 4. The saturation magnetizations ($4\pi M_s$) of the system $Sm_2(Co_{1-x-y}Fe_xMn_y)_{17}$ for y=0 and y=0.059 at room and liquid helium temperatures as a function of the fraction of cobalt atoms replaced (x+y).

4.2 K and 300 K is approximately triple that of the quaternary curves. The composition dependence of $4\pi M_s$ is also less marked for the quaternaries. The present values of $4\pi M_s$ and other parameters were compared[16] with those obtained in previous investigations. Agreement in $4\pi M_s$ is reasonable as, for the most part, individual measurements fall within ± 5% of the mean for the various sets of results. This agreement in $4\pi M_s$ contrasts sharply with the lack of agreement for the H_A^o values which we have already attributed to the long extrapolations used by previous investigators.

In Figures 5A and 5B the magnetocrystalline anisotropy contants K_1 derived from our H_A values for temperatures of 4.2 K and 300 K for the $Sm_2(Co_{1-x}Fe_x)_{17}$ alloys. These are compared with the corresponding P-S results. P-S obtained their low temperature points by extrapolating from 77 K. Thus, their results involve both temperature and field extrapolations. It is of interest to note that while our 300 K results have qualitatively the same variation with composition as do those of P-S, the low temperature sets of results are quite different. In particular, our results show a drop, occurring in the region $0.1 \leq x \leq 0.2$, from a constant level at $K_1(0) = 6.4\times10^6 Jm^{-3}$ for $x < 0.1$ to another level at $K_1(0) = 5.1\times10^6 Jm^{-3}$ for $x \geq 0.2$. This contrasts with the monotonic decrease in $K_1(0)$ for the P-S work. Figure 5A also reproduces the P-S results[1,18] for $K_1(0)$ of the $Y_2(Co_{1-x}Fe_x)_{17}$ system. These latter results involve only the temperature extrapolation, since the yttrium system was saturated by the 17 kOe available to P-S[18].

The excess anisotropy energy $\Delta K_1(0) = K_1(0)^{Sm} - K_1(0)^{Y}$, derived from Figure 5A, is shown in Figure 6. Of course, the contrasts with the P-S work, seen in Figure 5A persist. However, for our work a sharp change in slope now occurs near x≈0.2. In order to obtain $\Delta K_1(0)$ for the quaternary system $Sm_2Mn(Co_{1-x}Fe_x)_{16}$, an estimation had to be made concerning $K_1(0)$ for the as-yet-not-studied $Y_2Mn(Co_{1-x}Fe_x)_{16}$ series of compounds. P-S had reported on the $Y_2(Co_{1-x}Mn_x)_{17}$ and $Y_2(Co_{1-x}Fe_x)_{17}$ compounds. Their work is shown in Figure 7, where it can be seen that the substitution of Mn for Co far more rapidly increases $K_1(0)$ than does the substitution of Fe. The difference between the $K_1(0)$ values for the Mn and Fe is approximately a constant ($0.66\times10^6 Jm^{-3}$) up to the maximum in the Mn curve at x=0.15. Therefore, it was decided to approximate the $K_1(0)$ dependence for the quaternary yttrium compound by adding to the Fe curve the difference at x=0.059 (corresponding to one atom of Mn or Fe). The resulting approximate curve is also shown in Figure 7. By combining these results with the $K_1(0)$ values for the quaternary $Sm_2Mn(Co_{1-x}Fe_x)_{16}$ series shown in Figure 8, the desired $\Delta K_1(0)$ information was obtained.

From the results in P-S[1], it can be shown that the crystal-field parameter $\langle r^2\rangle A_2^o$ is related to the stabilization energy or excess anisotropy energy $\Delta K_1(0)$ by the expression

$$\langle r^2\rangle A_2^o = \frac{\Delta K_1^T(0)}{0.618}, \qquad (2)$$

1. R. S. Perkins and S. Strässler, Phys. Rev. B15, 477 (1977).

16. H. A. Leupold, F. Rothwarf, J. J. Winter, A. Tauber, J. T. Breslin, and A. Schwartz, Proc. of the Second International Symposium on Mangetic Coercivity and Anistropy of Rare Earth-Transition Metal Alloys, Univ. of California, San Diego, July 1, 1978; printed by Univ. of Dayton School of Engineering, K. J. Strnat, Ed., p. 87.

18. R. S. Perkins and H. Nagel, Physica 80B, 143, (1975).

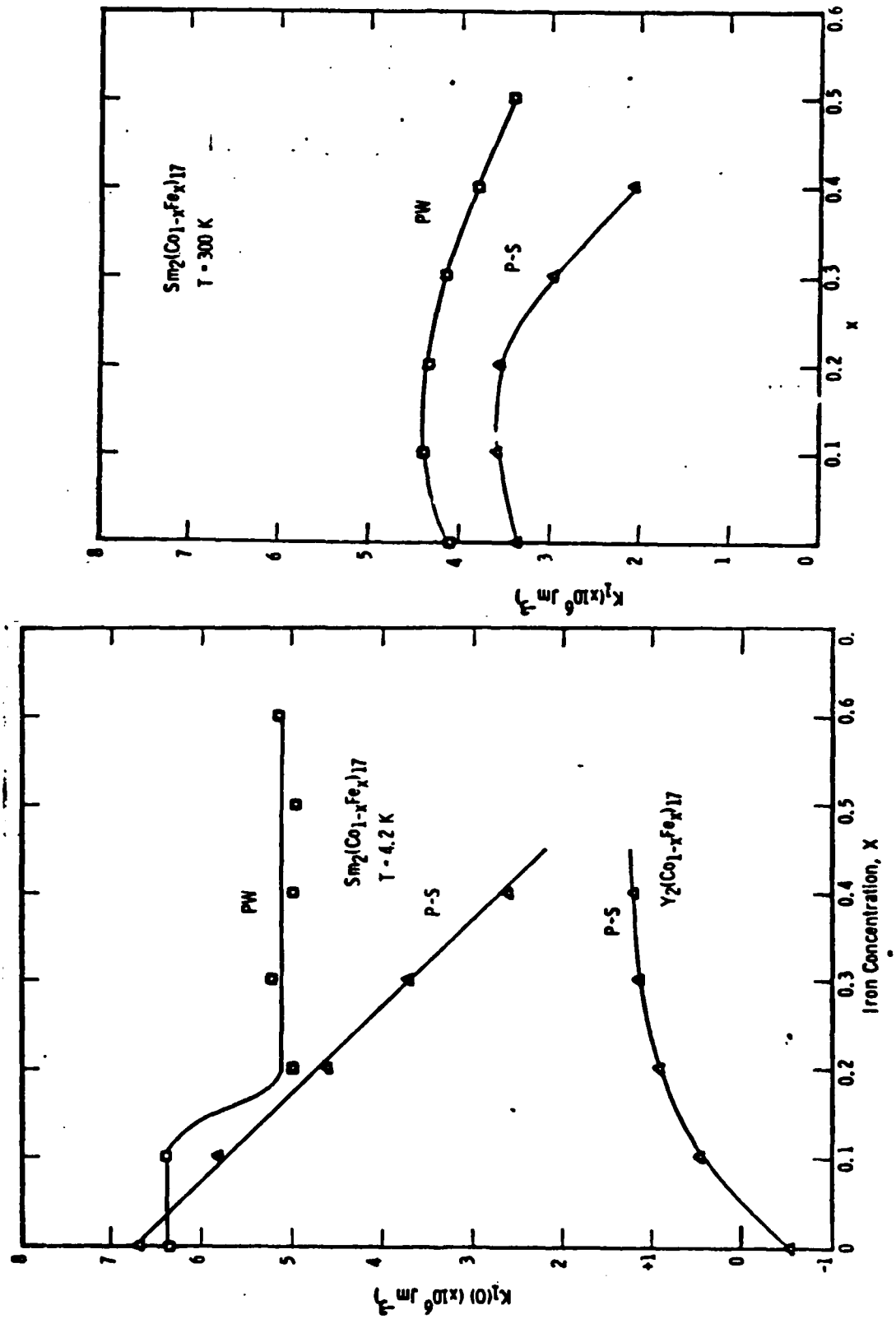

Figure 5. The anisotropy constants ($K_1=H_AM_s/2$) for the system $Sm_2(Co_{1-x-y}Fe_xMn_y)_{17}$ at liquid helium (A) and room (B) temperatures. The results of the present work (PW) are compared with those obtained by Perkins and Strässler[1] (P-S) on extraplation from H≈20 kOe. The P-S results for the $Y_2(Co_{1-x}Fe_x)_{17}$ system are also shown in (A).

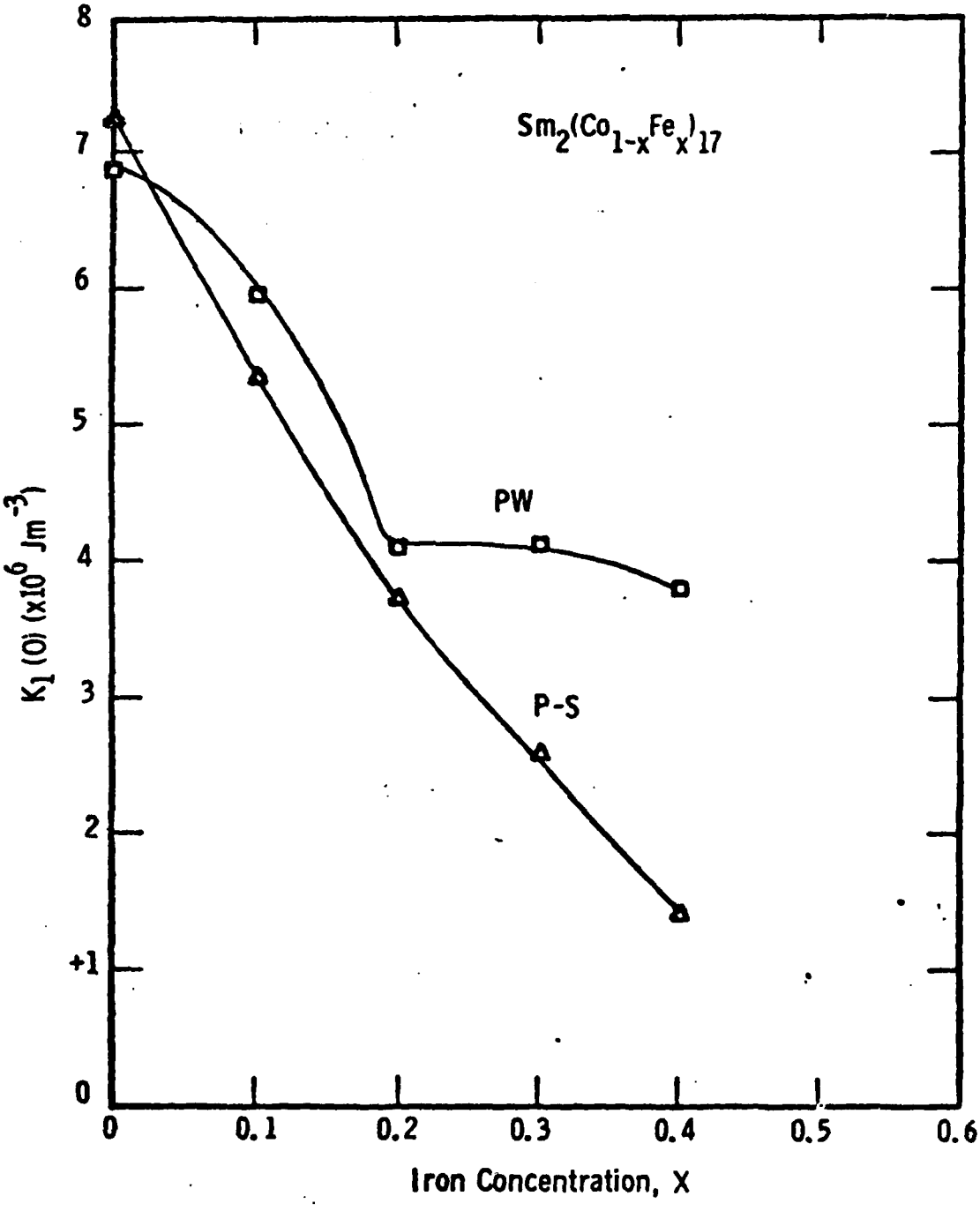

Figure 6. The composition dependence of the stabilization energy $\Delta K_1(0)$ at liquid helium temperature of the system $Sm_2(Co_{1-x}Fe_x)_{17}$ for the present work (PW) and that of Perkins and Strässler[1] (P-S).

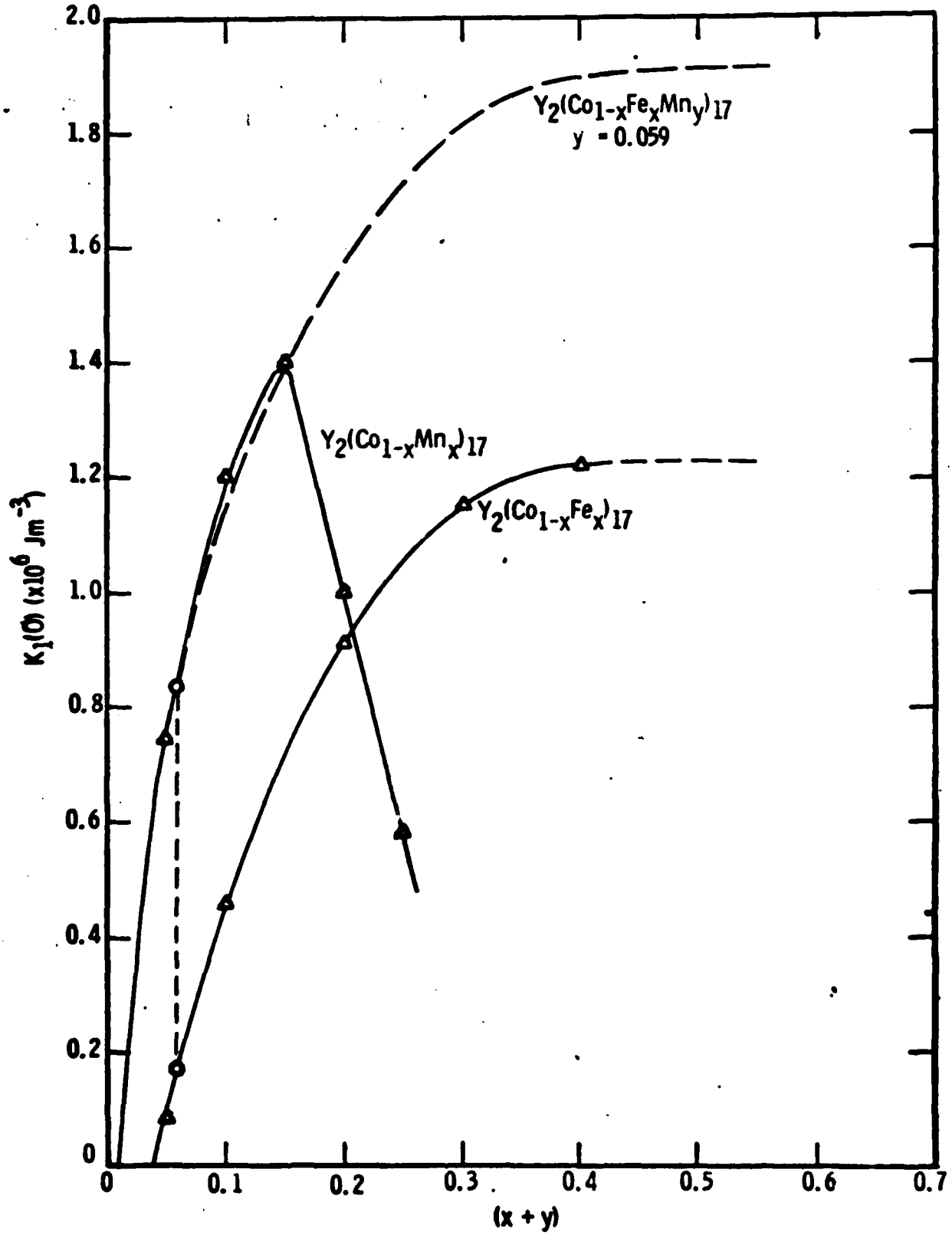

Figure 7. The anisotropy constants $K_1(0)$ at liquid helium temperature for the system $Y_2(Co_{1-x-y}Fe_xMn_y)_{17}$, (Y=0.059) for the systems $Y_2(Co_{1-x}Mn_x)17$ and $Y_2(Co_{1-x}Fe_x)17$.

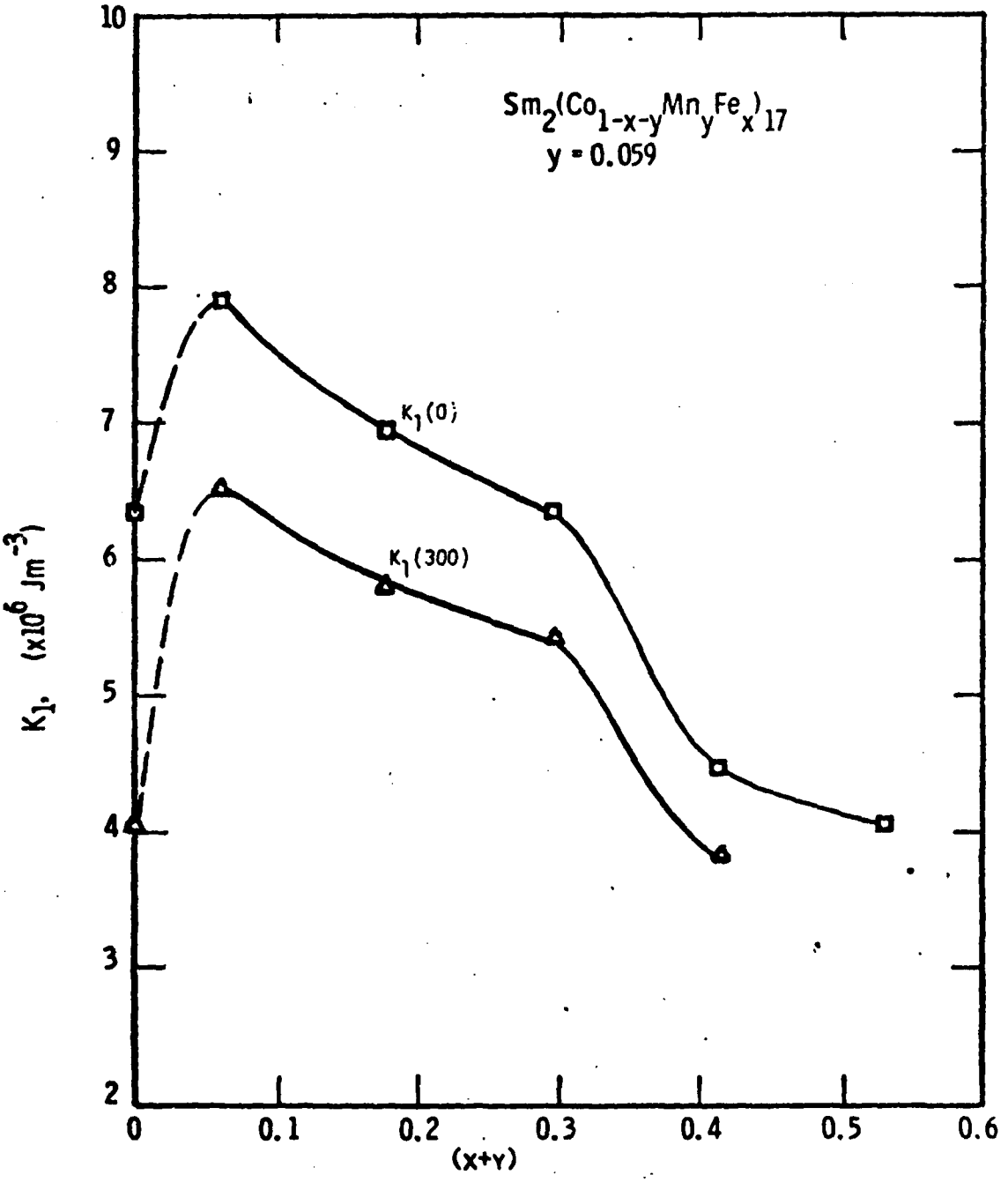

Figure 8. The composition dependence of the anisotropy constant $K_1(0)$ at liquid helium temperature of the system $Sm_2(Co_{1-x-y}Fe_xMn_y)_{17}$, (Y=0.059).

where both $\langle r^2 \rangle A_2^0$ and $\Delta K_1^T(0)$ are given in temperature units, and the factor of 0.618 has already been discussed by P-S. The conversion of the excess anisotropy energy per unit volume $\Delta K_1^E(0)$, which has been shown in the various figures, into temperature units is given by

$$\Delta K_1^T(0) = \frac{\Delta K_1^E(0) M}{2\rho k_B N_A} \quad , \tag{3}$$

where M is the molecular weight; ρ, the density; k, Boltzmann's constant; and N_A, Avogadro's number. The factor of 2 converts the results to a per samarium ion basis. The final crystal-field parameter results for the two systems studied are shown in Figure 9.

DISCUSSION

The $Sm_2(Co_{1-x}Fe_x)_{17}$ System

The present work shows that the anisotropy fields H_A are significantly higher than had been previously estimated in the work of P-S[1] (see Figure 1). Since P-S[1] have deduced extensive physical consequences from their results, our discussion is directed primarily to a comparison of our work with theirs. Our magnetization measurements, Figure 4, were essentially in agreement with those of P-S. The combination of the anisotropy and magnetization data led to the anisotropy constants K_1, shown in Figure 5, where significant differences from the previous values of P-S are apparent, especially at the liquid helium temperature. Whereas the K_1 variations with composition for the two studies are similar at 300 K, there is a significant difference in the low temperature functions. This difference is reflected in the stabilization energy $\Delta K_1(0)$ and crystal-field parameter $-\langle r^2 \rangle A_2^0$ functions shown in Figures 6 and 9. These discrepancies between the two studies are attributed to the H_A underestimations due to the large field extrapolations used in the P-S work.

Our work displays a sharp change in slope at $x \simeq 0.2$ for both $\Delta K_1(0)$ and $-\langle r^2 \rangle A_2^0$, seen in Figures 6 and 9, together with the steep fall of their values in the interval $0<x<0.2$. These results point to the possibility for a preferential substitution of Fe into one of the four possible cobalt sites in the $R\bar{3}m$ rhombohedral structure characteristic of these 2-17 compounds.[6] Such an interpretation is consistent with previous evidence[19-23] for a nonstatistical distribution of Fe on

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23. J. Déportes, D. Givord, R. Lemaire, H. Nagai and Y. T. Yang, J. Less-Comman Metals 44, 273 (1976).

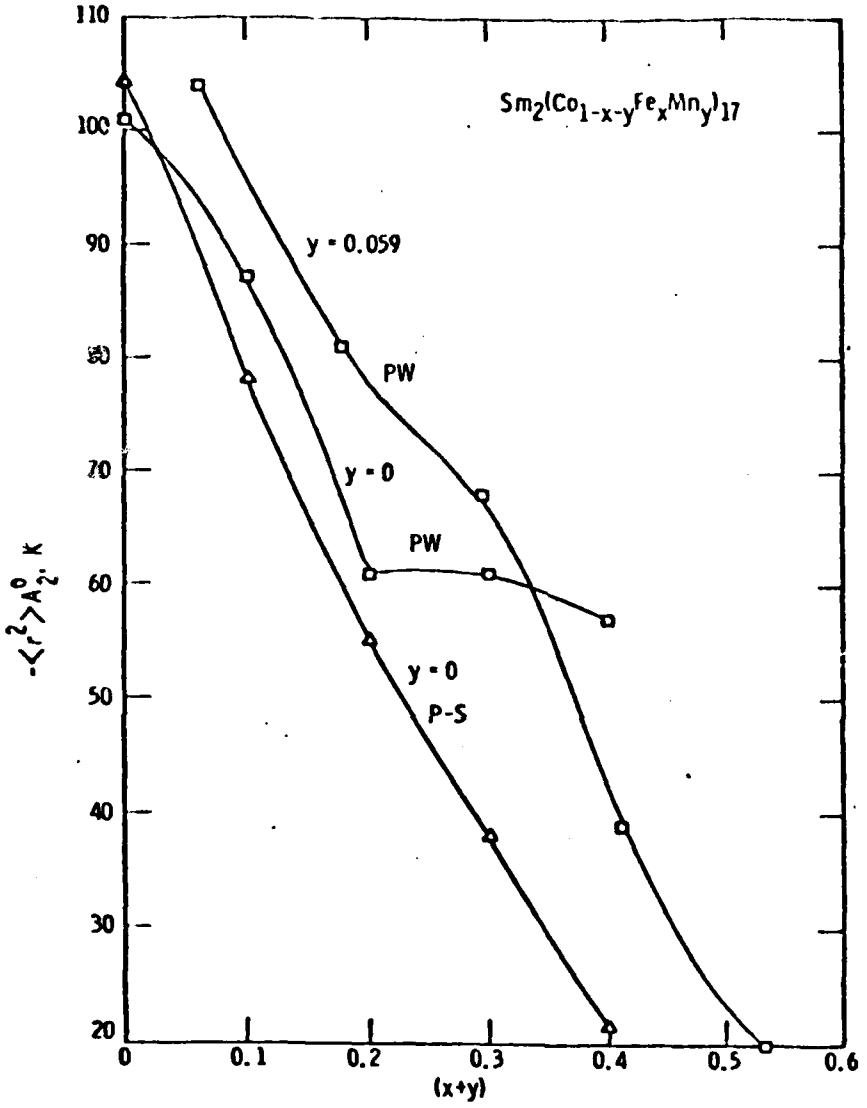

Figure 9. The composition dependence of the crystal field parameter $-\langle r^2\rangle A^0_2$ of the system $Sm_2(Co_{1-x-y}Fe_xMn_y)_{17}$, (Y=0 and Y=0.059) for the present work (PW) and that of Perkins and Strässler[1] (P-S) for Y=0.

the transition metal sites in 2-17 compounds. Perkins and Fischer[19] inferred such behavior from a study of two compounds in the $Y_2(Co_{1-x}Fe_x)_{17}$ system. They concluded that Fe prefers the 6c dumbbell sites but avoids the 18f sites. Inomata[20] did a detailed spin echo NMR study of both the $Y_2(Co_{1-x}Fe_x)_{17}$ and $Y(Co_{1-y}Fe_y)_5$ systems. The NMR behavior as a function of composition of $Y_2(Co_{1-x}Fe_x)_{17}$ differs significantly from that of $Y(Co_{1-y}Fe_y)_5$. This is interpreted as resulting from a strong antiferromagnetic exchange interaction of Fe-Fe pairs occupying 6c sites. Inomata concludes that substitution of iron for cobalt in $Y_2(Co_{1-x}Fe_x)_{17}$ initially occurs mainly at the 6c sites. Subsequently, at higher concentrations iron enters the 18h sites in preference to the 18f sites. He also finds that such a model explains the composition dependence of the magnetic anisotropy in $Y_2(Co_{1-x}Fe_x)_{17}$ seen by Katayama and Shikata[21] which is the same as that seen by Perkins and Nagel.[18] Further evidence for the preferential substitution of iron into the 6c sites of 2-17 compounds is found in the Mössbauer study of $Tm_2(Co_{1-x}Fe_x)_{17}$ by Gubbens, van der Kraan and Buschow.[22] They also explain the magnetic anisotropy[18,21] of the $Y_2(Co_{1-x}Fe_x)_{17}$ system by assuming that a similar site preference by iron applies quite generally to compounds of the type $R_2(Co_{1-x}Fe_x)_{17}$. Further evidence for the preferential substitution of iron atoms into the rhombohedral structure of $Y_2(Co_{1-x}Fe_x)_{17}$ ternaries is found in the neutron diffraction results of Déportes et al.[23] Narasimhan and Wallace[24] reach similar conclusions about the preferential site occupation by iron from their magnetic anisotropy studies of the systems $Tm_2(Co_{1-x}Fe_x)_{17}$ and $Er_x(Co_{1-x}Fe_x)_{17}$. Thus, the initial decrease in stabilization energy with iron concentration seen in our work (Figure 6) seems to correlate well with 6c site occupation, while sharp change in slope at x 0.2 may be indicative of the completion of 6c site occupation and the subsequent onset of more preferential occupation of the 18h sites.

It is useful to recapitulate Inomato's explanation of the $Y_2(Co_{1-x}Fe)_{17}$ magnetic anisotropy K_1 composition dependence, so as to better consider our room temperature and liquid helium K_1 results for the $Sm_2(Co_{1-x}Fe_x)_{17}$ system. On the basis of a point charge model for calculating the magnetic anisotropy of Y_2Co_{17}, Inomata points out that the contributions from the 6c, 18h and 9d cobalt sites are

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P.C.M. Gubbens, A.M. van der Kraan, and K.H.J. Buschow, Solid State Commun. 19, 355 (1976).

23. J. Déportes, D. Givord, R. Lemaire, H. Nagai and Y.T. Yang, J. Less, Common Metals 44, 273 (1976).

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negative while those of the 18f sites are positive. Thus, Y_2Co_{17} has a negative anisotropy constant.[1] When Fe enters preferentially into the 6c sites, K_1 becomes increasingly positive[1] until it reaches a maximum when the three negative sites are nearly filled at x 0.4. When additional Fe is added, the positive 18f sites begin to be occupied and K_1 rapidly falls to a large negative value characteristic of Y_2Fe_{17}. If one uses this model to explain what happens to Sm_2Co_{17}, one would again expect an initial increase in K_1 as iron is substituted for cobalt. In fact, this is just what is shown in Figure 5B for both our work and that of P-S at room temperature. A broad, shallow maximum occurs near x 0.2. However, the low temperature results seen in Figure 5A show that $K_1(0)$ decreases from one plateau to another in the interval 0.1 x 0.2. An explanation that presents itself is that different temperature dependences exist for the anisotropy contributions from each site such that a sharp drop in K_1 develops at low temperature when the 6c sites are nearly filled. Mössbauer and NMR studies of this system are being initiated in an attempt to clarify this problem.

The $Sm_2(Co_{1-x}Mn_x)_{17}$ System

Perkins and Strässler[1] have shown that as the Mn concentration is increased in the system $Sm_2(Co_{1-x}Mn_x)_{17}$, the anisotropy constant $K_1(0)$ initially decreases. The find that $K_1(0)$ has the values of 6.6×10^6 and $6.0\times10^6 Jm^{-3}$ for the respective concentrations x=0 and x=0.059. This contrasts with the increase in $K_1(0)$ from 6.3×10^6 to $7.9\times10^6 Jm^{-3}$ which we have obtained (see Figure 8). Again, we attribute the discrepancy between our results to the uncertainties introduced by the long extrapolations used in the P-S work. Our result is consistent with the valid Perkins and Strassler $K_1(0)$ data for the $Y_2(Co_{1-x}Mn_x)_{17}$ and $Y_2(Co_{1-x}Fe_x)_{17}$ compounds, shown in Figure 7. For these results no long extrapolations were involved. It can be seen that the substitution of Mn for Co far more rapidly increases $K_1(0)$ than does the substitution of Fe.

At room temperature (300 K) both studies yield increasing $K_1(300)$ values for the initial substitution of one maganese atom. Thus, $K_1(300)$ increases from 3.3×10^6 to $4.4\times10^6 Jm^{-3}$ at the concentrations x=0 and x=0.059 in the P-S study, while our results increase from 4.0×10^6 to $6.4\times10^6 Jm^{-3}$. Our result of enhanced anisotropy on initial manganese substitution is, therefore, consistent with the Inomata model for magnetic anisotropy. It also agrees with the conclusions of P-S that the preference for the 6c site and avoidance of the 18f site should increase in the order Fe< Mn. Again, one might argue for some change in the temperature dependences for the anisotropy contributions from each cobalt site, since at low temperatures the rate of increase of K_1 with Mn concentration is less than it is at room temperature. However, the effect is far less pronounced for the Mn than it was for the Fe substitution.

The $Sm_2(Co_{1-x-v}Fe_xMn_y)_{17}$

The substitution of one manganese atom for cobalt in the $Sm_2(Co_{1-x}Fe_x)_{17}$ system results in significant enhancement of the anisotropy field as can be seen in Figure 3. This enhancement is as much as 40% at 4.2 K and 55% at 300 K in the composition range $0 < (x+y) < 0.4$, with the greatest improvement occurring at x=0 for y=0.059 which corresponds to the substitution of the one manganese atom and no iron. The effect of the manganese substitution on $4\pi M_s$ is shown in Figure 4. The manganese causes an initial lowering at $4\pi M_s$ at 4.2 K (-9.3%), while there is no initial

1. R. S. Perkins and S. Strässler, Phys. Rev. B15, 477 (1977).

decrease at 300 K. Furthermore, the presence of the manganese causes a smaller change in magnetization as a function of increasing iron concentration. The combination of the anisotropy and magnetization data leads to the anisotropy constants shown in Figure 8. After an initial sharp rise in $K_1(0)$, when one Mn atom is substituted for a cobalt atom, there is a monotonic decline in $K_1(0)$ as iron is added. This is followed by a somewhat sharp change in slope at $(x+y)\approx 0.3$. It is of interest to note that the functional dependence of K_1 with iron concentration remains quite similar for 4.2 K and 300 K (Figure 8). The presence of the one Mn atom seems to have somewhat stabilized one or more of the various temperature dependent sublattice contributions to the anisotropy, so that the functional dependence of K_1 with iron remains the same at both 4.2 K and 300 K, in contrast to the case of no Mn (see Figure 5). Of course, the crystal field parameter curve (Figure 9) shows an enhancement as a result of the Mn substitution and also displays an inflection point in the interval $0.2 < (x+y) < 0.3$. This inflection point may now also reflect the completion of 6c site occupation and the subsequent onset of more preferential occupation of the 18h sites. Again, the recently initiated Mossbauer and NMR studies may clarify the situation.

The saturation magnetization of Sm_2MnCo_{16} shows significantly less temperature dependence than does either $SmCo_5$ or Sm_2Co_{17}, with a fractional increase of $4\pi M_s$ on going from 300 K to 4.2 K of only 5%, as compared to the respective values for the latter compounds of 11% and 16%. This result is somewhat surprising in view of the results of Perkins and Strassler,[25] who found a higher Curie temperature for Sm_2Co_{17} (1200 K) than for Sm_2MnCo_{16} (1100 K). In general, the Mn-based quaternary system $Sm_2Mn(Co_{1-x}Fe_x)_{16}$ displays about one third of the increase in $4\pi M_s$ found for the $Sm_2(Co_{1-x}Fe_x)_{17}$ system on reducing temperature from 300 K to 4.2 K (see Figure 4). This result may again be a consequence of some special influence that the presence of the Mn atom has on the temperature dependence of cobalt sublattice contributions to the magnetization.

A certain combination of properties is required to qualify a ferromagnetic material for use in permanent magnets.[26] First, a high room temperature saturation magnetization $4\pi M_s$ is needed to insure the availability of a useful remanent flux. The theoretical upper limit of the energy product, $(BH)_{max} = (2\pi M_s)^2$ in CGS units, is also determined by M_s. Second, a high Curie temperature, T_c, is required. Finally, to practically attain an energy product close to the theoretical limit, a sufficiently high intrinsic coerce is necessary, namely, $H_{ci} \geq 2\pi M_s$. The $Sm_2(Co_{1-x}Fe_x)_{16}$ system has room temperature $4\pi M_s$ values greater than 12 kG, and thus has the potential of attaining energy products in excess of 36 MGOe. The Curie temperatures are reasonably high (> 1000 K) for $x \leq 0.3$. Of course, the present work has demonstrated (Figure 3) that fairly high room temperature anisotropy fields (135 kOe $> H_A >$ 110 kOe) exist for $0 < x < 0.3$. If one applies the rule of thumb that the practically attainable intrinsic coercivity, H_{ci}, is the order of one tenth H_A, then one would expect an H_{ci} of approximately 11-13 kOe for properly prepared magnets of these materials. Therefore, these quaternary compounds more than satisfy the necessary condition that H_{ci} exceed $2\pi M_s$ (6 kOe), indicating that the theoretical energy product may be achieved. Thus, it is expected that these materials may well yield good permanent magnets with energy products in excess of 30 MGOe. Recently, Nagel[27] published evidence that supports this expectation. He

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26. Karl J. Strnat, IEEE Transactions on Magnetics MAG-8, 511 (1972).

27. H. Nagle, AIP Conf. Proc. 29, 603 (1976).

reported a remanence B_r of 10.6 kG and an H_{ci} of 13.4 kOe for a $Sm_2(Co_{0.8}Fe_{0.075}Mn_{0.125})_{17}$ sintered alloy. This corresponded to an energy product of 28 MGOe. The presence of two Mn atoms has reduced the magnetization as compared to the case for one Mn atom. Consequently, the energy product is lower than that projected above. Nevertheless, the result is quite encouraging. An effort is now underway to make actual magnets from the most promising of the $Sm_2Mn(Co_{1-x}Fe_x)_{16}$ compounds.

CONCLUSIONS

It is now clear from our measurements that the discrepancies with respect to the anisotropy fields H_A of $SmCo_5$[7,28-30] and Sm_2Co_{17}[5,7,8] that exist in the literature are a result of unwarranted extrapolations to high magnetic fields. Usually, the published H_A values are too low since the extrapolations, based upon insufficient applied field, fall well below the actual values obtained by the saturation of materials at high fields. Thus, some care should be taken when anisotropy data is employed in theoretical calculations [1,25,31] of magnetic parameters. Since most of such data in the literature are probably underestimations, the numerical values derived for the anisotropy constants and the crystal field parameters, for example, may be too low and may also mask or distort any compositional dependence that might be present. Such situations are illustrated in Figure 5 for the anisotropy constants and in Figure 6 for the stabilization energies of the $Sm_2(Co_{1-x}Fe_x)_{17}$ compounds.

The present experiments give some evidence for a preferential occupation of the various cobalt sublattice sites as Fe or Mn is substituted for Co. Furthermore, there is some evidence that the various cobalt sublattices make different temperature dependent contributions to the anisotropy. It seems that detailed Mössbauer and spin echo NMR studies [32,33] would be useful in elucidating these effects. In particular, an NMR study such as Inomata[20] made of the $Y_2(Co,Fe)_{17}$ and $Y(Co,Fe)_5$ systems might be fruitful.

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Finally, our study points to the possibility that technologically important permanent magnets with energy products in excess of 30 MGOe might be attainable with properly processed compounds of low Fe concentration in the $Sm_2Mn(Co_{1-x}Fe_x)_{16}$ system. Such magnets promise to have many important commercial and military applications.[2,3]

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